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## (54) INDIUM OXIDE-TIN OXIDE POWDER AND ITS PRODUCTION

### (57)Abstract:

**PROBLEM TO BE SOLVED:** To produce ITO powder capable of reducing nitrogen load such a ammonia in waste water, excellent in sinterability and containing alkali metals, or the like, in low contents, which is composed of primary particles having a uniform size and is almost free from aggregation between the primary particles, and further, by which a highly dense ITO sintered body is obtained.

**SOLUTION:** In a method for producing the indium oxide-tin oxide powder, which comprises mixing a solution of an indium salt, a solution of a tin salt and an alkali solution to form a precipitate containing indium and tin, separating a solid from liquid, washing and drying the obtained precipitate and firing the resultant precipitate, a solution of an alkali hydroxide is used as the alkali solution, the content of the alkali metal contained in the dried precipitate is controlled to be not more than 200 ppm, and the firing is carried out in an atmosphere gas containing a gaseous hydrogen halide or a gaseous halogen in an amount of  $\geq 1$  vol.% at 600 to 1,300°C and the fired material is washed with water.

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**CLAIMS**

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**[Claim(s)]**

[Claim 1] After making the precipitate which mixes the water solution, tin salt water solution, and alkali water solution of an indium salt, and contains an indium and tin generate, In the manufacture approach of the indium oxide-tin oxide powder by calcinating, after drying solid liquid separation and the precipitate washed and obtained An alkali water solution is a hydroxylation alkali water solution, and the alkali-metal content of the precipitate after drying is 200 ppm or less. The manufacture approach of indium oxide-tin oxide powder that the alkali-metal content characterized by washing with water after performing this baking below 600 degrees C or more 1300 degrees C in the controlled atmosphere which contains hydrogen halide gas or halogen gas more than 1 volume % is 10 ppm or less.

[Claim 2] The manufacture approach according to claim 1 that the alkali-metal content of precipitate after desiccation is 100 ppm or less.

[Claim 3] The manufacture approach according to claim 1 or 2 supplied so that the approach of mixing the water solution, tin salt water solution, and alkali water solution of an indium salt may be maintained by 40-degree-C or more underwater [ less than 100-degree C ] and pH under reaction may be maintained in or more 4 seven or less range in the mixed water solution and hydroxylation alkali water solution of an indium salt and tin salt.

[Claim 4] The manufacture approach according to claim 3 supplied so that pH under reaction may be maintained in or more 5 six or less range.

[Claim 5] The manufacture approach according to claim 1 to 4 calcinated below 800 degrees C or more 1200 degrees C.

[Claim 6] The manufacture approach according to claim 1 to 5 cracked after calcinating and washing with water.

[Claim 7] The manufacture approach according to claim 1 to 6 that an alkali-metal content is 1 ppm or less.

[Claim 8] The manufacture approach according to claim 1 to 7 that hydroxylation alkali water solutions are a sodium hydroxide and a potassium hydroxide.

[Claim 9] The content of tin oxide manufactured by the approach according to claim 1 to 8 is 2 - 20 % of the weight, and the diameter of a BET specific surface area is a certain indium oxide-tin oxide powder 0.05-micrometer or more 1 micrometer or less and 99.99 % of the weight or more of purity.

[Claim 10] Indium oxide-tin oxide powder according to claim 9 whose diameter of a BET specific surface area is 0.1 micrometers or more 0.5 micrometers or less.

[Claim 11] For 2 - 20 % of the weight, and the diameter of a BET specific surface area, the diameter of 50% of 0.05-micrometer or more 1 micrometer or less and accumulation particle size distribution is [ the content of tin oxide manufactured by the approach according to claim 6 ] a certain indium oxide-tin oxide powder 1 micrometer or less.

[Claim 12] Indium oxide-tin oxide powder according to claim 11 whose diameter of a BET specific surface area is 0.1 micrometers or more 0.5 micrometers or less.

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**DETAILED DESCRIPTION**

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**[Detailed Description of the Invention]****[0001]**

[Field of the Invention] This invention has the conductivity which was excellent with high transparency, and relates to the transparent conductive fine particles for which the reflexivity over the electromagnetic wave as [ electric contact or the object for circuits ] and is highly used also as an object for electromagnetic wave shielding, and its manufacture approach.

**[0002]**

[Description of the Prior Art] The tin dope indium oxide which added diacid-ized tin ( $\text{SnO}_2$ ) as an impurity to 3 indium oxide ( $\text{In}_2\text{O}_3$ ) as a transparent conductive ingredient which has high conductivity with such high transparency conventionally is known. To the light, while this tin dope indium oxide is transparent,  $\text{Sn}^{4+}$  by the diacid-ized tin ( $\text{SnO}_2$ ) which is the semi-conductor in which the conductivity of an oxygen deficiency mold is shown, and was added by coincidence becomes the source of supply of a free electron, i.e., a donor, and it is accumulated in the donor level near the conduction band lower limit, and gives high conductivity.

[0003] Moreover, although the spray method to which gaseous phase reaction is made to carry out as a means to obtain such tin dope indium oxide as a membrane, using the solution of the indium 111 trichloride ( $\text{InCl}_3$ ) which added sputtering, vacuum evaporation technique, or a tin tetrachloride ( $\text{SnCl}_4$ ) is known As a concrete means to obtain fine particles, the mixed solution of the indium 111 trichloride ( $\text{InCl}_3$ ) and a tin tetrachloride ( $\text{SnCl}_4$ ) is dropped at the solution of an ammonium carbonate. The coprecipitation hydroxide of an indium and tin is made to generate, this coprecipitation hydroxide is rinsed with a decantation or a centrifuge method, and it dries, and further, after carrying out heating reduction of this dry matter within a hydrogen ambient atmosphere or a vacuum ambient atmosphere, the reduction baking approach to pulverize is learned.

**[0004]**

[Problem(s) to be Solved by the Invention] However, in order to take measures, like what processed low resistance-ization in order to heighten a shielding effect conventionally makes burning temperature high, sintering progresses and condensation starts a maldistribution violently. These had the problem of depositing in a coating. Moreover, there was that [ no ] by which a green paint film is obtained with sufficient distribution from the blue excellent in translucency. As mentioned above, good fine particles were not obtained in any of conductivity and dispersibility. This invention aims at offer of the transparent conductive fine particles which show higher conductivity and good dispersibility, and offer of the suitable manufacture approach for it in view of such a conventional trouble.

**[0005]**

[Means for Solving the Problem] When this invention person inquired wholeheartedly in order to solve this technical problem, by replacing with the conventional tetravalent compound of a tin raw material, and using a divalent compound for the doping agent added to an indium as a means to obtain low resistance, he could acquire reducing atmosphere easily, and  $\text{O}_2$  deficit increased, and he found out that low resistance was realizable.

[0006] Namely, Sn content of this invention is 0.1 - 30 % of the weight in SnO<sub>2</sub> conversion the 1st. Tin dope indium oxide powder characterized by color tones being x values of 0.280-0.370, and y value of 0.316-0.400 on xy chromaticity diagram; to the 2nd Specific surface area Tin dope indium oxide powder characterized by the F-potential which Sn content measured in 0.01molKCl water solution at 0.1 - 30 % of the weight by SnO<sub>2</sub> conversion being +5mV or more; above 15m<sup>2</sup>/g [ 3rd ] By 10-30nm, the Maine peak half peak width near 2 theta= 30.5 degree on an X diffraction Fig. at 0.2 degrees - 0.7 degrees [ particle size ] Tin dope indium oxide powder characterized by the rate of volume resistivity being below 3x10<sup>11</sup>-ohmcm in the condition of the green compact fabricated by the pressure of 200kg/cm<sup>2</sup>; to the 4th It is made to dry, after adding an ammonium carbonate to the acidic solution which dissolved an indium and divalent tin and making it generate the coprecipitation hydroxide of an indium and tin. The manufacture approach of the tin dope oxidization Inn Jim powder characterized by calcinating this coprecipitation hydroxide at 500-800 degrees C by the inert gas ambient atmosphere containing moisture; to the 5th Said 4th [ the ] characterized by supply of the inert gas ambient atmosphere containing said moisture being a flow rate more than 1.0 ml/min-g (per-minute amount of supply per 1g of desiccation coprecipitation hydroxides) is provided with the manufacture approach of the tin dope indium oxide powder a publication.

[0007]

[Embodiment of the Invention] In this invention, a fusibility indium compound and a divalent fusibility tin compound are used as starting material. As a fusibility indium compound, InCl<sub>3</sub> is used, for example. This InCl<sub>3</sub> is easily obtained by carrying out the heating dissolution of the indium metal in a hydrochloric-acid acidic solution. As a fusibility tin compound, SnCl<sub>2</sub> is used, for example. SnCl<sub>2</sub> melts tin metal to a hydrochloric acid, and is obtained, and if this solution is condensed, two stable monohydrates will be obtained. By using a divalent tin compound (for example, SnCl<sub>2</sub>), sufficient reducing atmosphere is acquired in a baking process, and oxygen deficiency sufficient in the crystal lattice of a baking object can be formed.

[0008] Said InCl<sub>3</sub> water solution and SnCl<sub>2</sub> water solution are mixed at a rate that Sn content in the tin dope indium oxide powder after baking becomes 0.1 - 30 % of the weight by SnO<sub>2</sub> conversion in order to obtain conductive high powder. The coprecipitation product of In(OH)<sub>3</sub> and Sn(OH)<sub>2</sub> is obtained by adding into this mixed liquor and making a hartshorn-salts solution, for example, the mixed alkaline solution of ammonium bicarbonate (NH<sub>4</sub>HCO<sub>3</sub>) and aqueous ammonia, stir and react to it. Making Sn content of tin dope indium oxide powder into 0.1 - 30 % of the weight by SnO<sub>2</sub> conversion here because high conductive powder with a high free electron consistency is obtained in this range, it is because good conductive powder will not be obtained if it separates from this range. As a means to acquire high dispersibility, an alkali solution is added in the mixed water solution of acid InCl<sub>3</sub> and SnCl<sub>2</sub> in the above-mentioned reaction process, a nucleation is carried out at a stretch in a neutral region, and while attaining equalization of a particle and making it distribute, generating of coarse grain is controlled. The high fine particles of translucency can be obtained by carrying out like this.

[0009] After washing the obtained coprecipitation product repeatedly several times by the decantation with warm water, it is made to dehydrate, and long duration desiccation is carried out at 150 more degrees C. Subsequently, baking processing is performed by holding the obtained desiccation grain material in an ambient atmosphere furnace, and holding the inert gas containing moisture to 500 degrees C - 800 degrees C high temperature with through for about several hours. Although nitrogen, an argon, carbon dioxide gas, etc. are usable as inert gas, nitrogen and an argon are desirable from the field of a property and costs, and especially nitrogen is desirable. A moisture content is added in inert gas so that a good color tone and dispersibility may be acquired. As a content of moisture, what is necessary is just saturated water vapor pressure extent in a room temperature. Within the limits of burning temperature of 500 degrees C - 800 degrees C is desirable. If less than 500 degrees C of baking are [ burning temperature ] insufficient, and resistance of the fine particles obtained becomes high and exceeds 800 degrees C, the dispersibility of the fine particles obtained by sintering and condensation progressing will serve as a defect.

[0010] Moreover, in a baking process, by carrying out the flow rate of aeration gas more than 1.0

ml/min-g (per-minute amount of supply per 1g of desiccation coprecipitation hydroxides), equalization of an ambient atmosphere can be attained, partial sintering can be controlled, and the powder which presents green can be obtained from blue with good dispersibility. If the flow rate of aeration gas is less than 1.0 ml/min-g, dispersion in an ambient atmosphere will be produced in a firing furnace, and it becomes property nonuniformity, and is not desirable.

[0011] The color tone of fine particles shall show x values of 0.280-0.370, and y value of 0.316-0.400 on xy chromaticity diagram. since the thing of this color tone does not almost have the light absorption near [ highest ] 500nm of the sensibility people's eyes in the light at blue - yellowish green and translucency is good -- it is -- x values and y value -- sufficient translucency will not be acquired, if one side separates from this range even if few. Underwater F-potential was measured as an index of the dispersibility of fine particles, and the stability in the inside of a solvent(water) was evaluated. When the F-potential of fine particles shows a forward value, preferably, at the time of +5mV or more, the fine particles in a coating show good dispersibility more preferably at the time of +15mV or more, and dispersibility with F-potential sufficient by zero or less is not acquired.

[0012] In order to acquire still more sufficient translucency, specific surface area is more preferably carried out to more than 30m<sup>2</sup>/g more than 15m<sup>2</sup>/g, and within the limits of particle size (primary particle size by the TEM photograph) of 10-30nm is desirable. The atomization of under 15m<sup>2</sup>/g is not enough as specific surface area, and sufficient translucency is not acquired. Moreover, sufficient translucency will not be acquired if it separates from the range whose particle size is 10-30nm. Furthermore, in order to acquire high conductivity, the half peak width (henceforth XRD half peak width) of the Maine peak near X diffraction Fig. upper 2 theta= 30.5 degree is preferably good [ the crystallinity of fine particles ] to consider [ 0.2 degrees - 0.7 degrees ] as within the limits of 0.3 degrees - 0.5 degrees more preferably. At less than 0.2 degrees, when sintering progresses, coarse-grain-ization arises, translucency is checked and it exceeds 0.7 degrees, crystallinity insufficient [ baking ] and sufficient is not acquired but conductivity serves as a defect. In order to obtain a high shielding effect, in the condition of the green compact fabricated by the pressure of 200kg/cm<sup>2</sup>, below 3x10<sup>1</sup>-ohmcm has a desirable rate of volume resistivity, and further 3x10<sup>1</sup> or less are more desirable.

[0013]

[Example] [Example 1] The heating dissolution of the indium metal was carried out with HCl acidity liquid, InCl<sub>3</sub> solution was obtained, SnCl<sub>2</sub> solution was added at a predetermined rate in this InCl<sub>3</sub> solution, and the mixed solution of pH 1-2 was made in it. It added to this mixed solution and the ammonium bicarbonate solution was made to stir and react to it. pH at the time of reaction termination is 6-7. The obtained coprecipitation product was dried at 150 degrees C for 20 hours, after washing repeatedly and filtering and dehydrating by five decantations with warm water 60 degrees C or more. Furthermore, this desiccation sample 400g was taught to the tubular ambient atmosphere furnace, and it calcinated at 550 degrees C for 3 hours, carrying out aeration of the N<sub>2</sub> gas by the flow rate of 10 ml/min-g (per-minute amount of supply per 1g of desiccation coprecipitation hydroxides). During aeration, humidity control was performed so that a part for 30-degree C saturated water might be maintained. The desk mill ground the obtained baking object.

[0014] ICP analysis performed measurement of Sn content. Primary particle size was measured with the transmission electron microscope (TEM). Specific surface area was measured by law one BET. The color tone was measured by double beam flicker photometry (color difference meter). The X diffraction was performed using the scintillation counter under conditions of 1 or 50kV of CuK-alpha. The rate of specific resistance of a green compact asked by performing resistance measurement with the four point probe method about the green compact fabricated by the pressure of 200kg/cm<sup>2</sup>. F-potential distributed fine particles ultrasonically (exposure during 5 minutes) in the 0.01-mol KCl water solution, and was measured with the applied voltage of 100V using the F-potential meter of a laser rotating-prism method.

[0015] Sn content of the fine particles obtained by the above approach was 5.3 % of the weight in SnO<sub>2</sub> conversion, particle size was 10nm and specific surface area was 56.5m<sup>2</sup>/g. These tin dope indium oxide fine particles had the color tone of a bluish green color, and x values and y values in xy chromaticity diagram were 0.323 and 0.353, respectively. Moreover, the XRD half peak width of these fine particles

was [ 0.1ohmcm and the F-potential of 0.58 degrees and the rate of volume resistivity of a green compact ] +25mV.

[0016] [Example 2] The same processing as an example 1 was performed except having replaced burning temperature with 550 degrees C, and having considered as 650 degrees C. Sn content of the obtained tin dope indium oxide fine particles was 5.3 % of the weight in \*\* SnO<sub>2</sub> conversion, particle size was 15nm and specific surface area was 43.1m<sup>2</sup>/g. These fine particles had the blue color tone, and x values and y values in xy chromaticity diagram were 0.301 and 0.317, respectively. Moreover, the XRD half peak width of these fine particles was [ 0.03ohmcm and the F-potential of 0.45 degrees and the rate of volume resistivity of a green compact ] +23mV.

[0017] [Example of a comparison] The heating dissolution of the indium metal was carried out with HCl acidity liquid, InCl<sub>3</sub> solution was obtained, SnCl<sub>2</sub> solution was added at a predetermined rate in this InCl<sub>3</sub> solution, and the mixed solution of pH 1-2 was made in it. It added in the ammonium bicarbonate solution and the aforementioned mixed solution was made to stir and react to it. pH at the time of reaction termination is 7. After having repeated the decantation 5 times, washing and filtering and dehydrating with warm water 60 degrees C or more about the obtained coprecipitation product, desiccation was performed at 150 degrees C for 20 hours. Furthermore, this desiccation sample 400g was taught to the tubular ambient atmosphere furnace, and it calcinated at 550 degrees C for 3 hours, carrying out aeration of the N<sub>2</sub> gas by the flow rate of 0.5 ml/min-g. Moisture was not added in aeration gas. The desk mill ground the obtained baking object. Sn content of the obtained fine particles was 5.3 % of the weight in SnO<sub>2</sub> conversion, and the particle size of 10nm and specific surface area were 58.0m<sup>2</sup>/g. These tin dope indium oxide fine particles had the yellow-green color tone, and x values and y values in xy chromaticity diagram were 0.380 and 0.383, respectively. Moreover, the XRD half peak width of these fine particles was [ 3.0ohmcm and the F-potential of 0.68 degrees and the rate of volume resistivity of a green compact ] -3.2mV.

[0018]

[Effect of the Invention] The transparent conductive fine particles which show high conductivity and high dispersibility in a high transparence region by this invention are obtained so that clearly from the above explanation. Moreover, without [ therefore ] needing the baking processing in strong reducing atmosphere, while being able to manufacture the aforementioned transparent conductive fine particles, the high running cost by an expensive facility or its facility is not needed, but the manufacture approach of economical transparent conductive fine particles with high safety can be offered.

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[Translation done.]